Hyperfine Interact (2007) 178:31–35
DOI 10.1007/s10751-008-9652-6

High temperature perturbed angular correlation studies of $Ln_2NiO_{4+\delta}$ Ln=La,Pr,Nd

J. Röder · M. Uhrmacher · K. D. Becker

Published online: 14 August 2008

Abstract High temperature measurements on $Ln_2NiO_{4+\delta}$ (Ln=La, Pr, Nd) have been performed indicating a complex behavior in PAC experiments which can be attributed to fluctuating electric field gradients caused by the high mobility of excess oxygen.

Keywords Perturbed angular correlation (PAC) · La_2NiO_4 · Pr_2NiO_4 · Nd_2NiO_4 · Hight temperature measurements

1 Introduction

$La_2NiO_{4+\delta}$ with the K_2NiF_4 type structure has been intensively studied since high temperature superconductivity was discovered in $La_2CuO_{4+\delta}$. Because of the mixed ionic and electronic conductivity with a large solubility for excess oxygen in $Ln_2NiO_{4+\delta}$, these materials are good candidates for a wide range of applications, such as cathodes for intermediate temperature solid oxide fuel cells (IT-SOFC), oxygen separators, oxygen pumps, or partial oxygen reactors. Experiments on these compounds have mostly been performed at moderate temperatures below 800°C.

J. Röder · K. D. Becker
Institute of Physical and Theoretical Chemistry,
Braunschweig University of Technology,
Braunschweig, Germany

J. Röder
e-mail: j.roeder@tu-bs.de

K. D. Becker
e-mail: k-d.becker@tu-bs.de

M. Uhrmacher (✉)
II. Institute of Physics, University of Göttingen, Göttingen, Germany
e-mail: muhrmac@gwdg.de

Although their structure is orthorhombic, no unique EFG can be observed in PAC experiments in the moderate or low temperature range. High temperature ^{111}In-PAC measurements up to 1,400°C, however, reveal the following: above 800°C two different fractions with well-defined frequencies appear. The temperature dependency of these fractions and of their EFGs was determined. The question will be discussed whether a smooth change of structural properties causes this observation or whether the phenomenon of motional narrowing in the concept of dynamical hyperfine interactions has to be invoked, see [1] and references cited therein.

2 Experiments

$Ln_2NiO_{4+\delta}$ (Ln=La, Pr, Nd) have been synthesized by a modified Peccini-method. Hydroxides have been precipitated from stoichiometric solutions of the metal nitrates and the organic base tetraethylammoniumhydroxide. The dried hydroxides were sintered at 1,000°C for 48 h and tempered at 600°C under pure oxygen for 6 h. Samples were characterized structurally by using a PW1820 X-ray diffractometer. The powders had crystallite sizes of about 60–80 nm. Pellets of 5 mm diameter were pressed from the powders. ^{111}In was implanted with 400 keV at IONAS/Göttingen into the pellets. Indium has a significant vapor pressure at temperatures above 700°C. Therefore, the samples have been sealed in small evacuated quartz tubes for the high-temperature measurements. Samples have been investigated in a wide temperature range from 9 to 1,673 K. The measurements were performed using a standard PAC-spectrometer equipped with NaI detectors.

3 Results

Although $La_2NiO_{4+\delta}$ is orthorhombic at room temperature, only strongly damped perturbation functions $R(t)$ are observed. Even after moderate annealing at 600°C, no changes occur. Also at temperatures as low as 9 K perturbation functions remain unchanged. All $R(t)$ have been fitted with a broad (90%) frequency distribution around 200 MHz at lower temperatures. However, above 800°C two sharp frequencies appear with fractions growing continuously with increasing temperature. This behavior is reversible. Figure 1 and Table 1 summarize these results.

$Pr_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$ were also studied and were found to exhibit a similar temperature dependence of the fractions. The two well-defined frequencies appear at significantly different temperatures in $Ln_2NiO_{4+\delta}$. At 1,200°C ν_Q values are found for Ln=Pr of about 173 and 195 MHz and for Ln=Nd of about 185 and 203 MHz.

In the last column of Table 1 we give the difference $\Delta=(\nu_{Q_2} - \nu_{Q_1})$ between the two sharp frequencies. In a rough estimate this difference is constant, independently of the measuring temperature, but the mean is clearly different for the three compounds. For Ln=La, Pr, and Nd we found the values of $\Delta = (\nu_{Q_2} - \nu_{Q_1}) = 30$, 22 and 16.5 MHz. In addition, the three compounds are found always to possess the higher fraction at the smaller frequency. The ratio of the two fractions at 1200°C ranges from 1,5 (La) to 3.5 (Pr) and 3.5 (Nd).

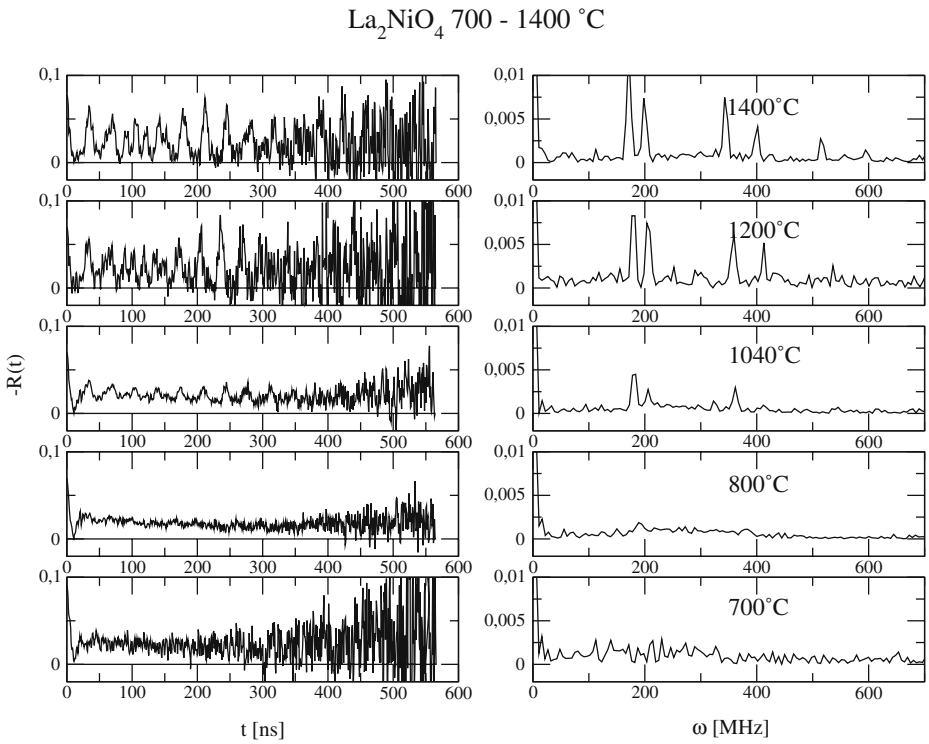

Fig. 1 ^{111}In/^{111}Cd PAC of $La_2NiO_{4+\delta}$ at different temperatures

Table 1 Fit-data of $La_2NiO_{4+\delta}$

T [°C]		Fraction [%]	ν_Q [MHz]	δ [MHz]	η	Δ [MHz]
800	1	2.4	177.5	8.893	0.0	
	2	6.8	202.4	2.554	0.0	24.9
	0	90.8	264.1	92.6	0.008	
1,040	1	15.6	191.4	1.034	0.050	
	2	7.9	219.0	2.472	0.001	27.6
	0	76.5	262.3	98.0	0.008	
1,200	1	50.8	197.0	0.630	0.008	
	2	35.0	226.4	0.0	0.009	29.4
	0	14.2	1.8	0.0	0.0	
1,400	1	56.7	189.0	0.785	0.001	
	2	29.8	219.7	0.075	0.009	30.7
	0	13.5	1.2	0.248	1.000	

4 Discussion

The understanding of these observations may be reached if the high amount of additional free oxygen ions in the lattice is taken into consideration in $Ln_2NiO_{4+\delta}$, δ =

0.16–0.18 [4]. The additional oxygen results in a torsion of the nickel octahedron. The experimental observations can be discussed in the context of dynamical interactions, which arise due to the high amount of highly mobile oxygen ions in these materials, even at lower temperatures. In the space group Fmmm there are at the top and bottom of each nickel octahedron five positions for additional oxygen atoms, which may result in a combination of 25 different electric field gradients, when symmetry effects get lost, because of also different neighbor positions of the other nickel octahedron. The $R(t)$ spectra show a strong damping at RT or at moderate elevated temperatures, which is a typical situation encountered in the presence of many different sites. At higher temperatures, the jump frequency of the oxygen ions increases which leads to the effect of motional narrowing where the ^{111}Cd probe detects only averaged EFG(s). Therefore, it is expected, that with increasing temperatures the fractions of existing unique EFGs increase and their frequencies get sharper, as it is seen here.

On the other hand, in these materials the solubility of oxygen decreases [2, 3] with increasing temperature. Evidently, the temperature range in which the stoichiometry tends to exact stoichiometry ($\delta = 0$) agrees with the temperature region where the two well-defined frequencies appear. Therefore, one might argue that at high temperatures there is no mobile oxygen left and the intrinsic EFGs of the Ln_2NiO_4 structure show up. To test this hypothesis we measured samples, which had been chemically reduced to get rid of additional oxygen. But the reduced material did not show the characteristic two sharp frequencies at lower temperatures. Instead, it showed a similar behavior as the oxidized samples, with only small changes in the $R(t)$ function.

Finally, the two observed EFGs have to be discussed. As their strength has a constant difference for each compound and their orientation is always axial, we assume that we observe a next neighbor atom with two different charge states. The high amount of excess oxygen needs a charge compensation, which is realized by Ni as a 2+ and a 3+ ion. Ni^{2+} should be the majority charge state, and in fact, the fraction with the smaller EFG is always the higher one. A similar argument was used to describe the two EFGs observed in Cr_2O_3 [6, 7], We therefore propose, that all probes are on the same site of the lattice, probably replacing the lanthanoide, as it was deduced for $La_2CuO_{4+\delta}$ by Saylor et al. [5]. The two different EFGs are caused by the presence of Ni^{2+} or Ni^{3+} in the neighborhood of the probes.

5 Conclusions

The Ruddlesden–Popper structures $Ln_2NiO_{4+\delta}$ (Ln=La, Pr, Nd) show a complex behavior in PAC experiments, which can be attributed to their oxygen excess and great oxygen conductivity. The strong damping of the $R(t)$ at room and moderate temperatures in an orthorhombic structure indicates a broad distribution of EFGs. Two different sites for ^{111}In observed at high temperatures due motional narrowing can be assigned to Ni^{2+} and Ni^{3+} in the neighborhood of the ^{111}Cd probe.

References

1. Uhrmacher, M.: Physica B **389**, 58 (2007)
2. Hayashi, A., Tamura, H., Ueda, Y.: Physica C **216**, 77–82 (1993)
3. Fernández-Díaz, M.T., Martínez, J.L., Rodríguez-Carvajal, J.: Solid State Ion. **63–65**, 902–906 (1993)
4. Jorgensen, D.J., Dabrowski, B., Shiyou, Pei, Richards, D.R., Hinks, D.G.: Phys. Rev. B **40**, 2187–2199 (1989)
5. Saylor, J., Takacs, L., Hohenemser, C., Budnick, J.I., Chamberland, B.: Phys. Rev. B **40**, 68854 (1989)
6. Neugebauer, M., Bartos, A., Lieb, K.P., Lupascu, D., Uhrmacher, M., Wenzel, Th.: Europhys. Lett. **29**, 175 (1995)
7. Vetter, U., Uhrmacher, M., Schwen, D., Lohstroh, A., Hofsss, H., Lieb, K.P.: Hyperfine Interact **136/137**, 607 (2001)